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METHODS FOR RELEASING METAL VAPORS  
IN THE UPPER ATMOSPHERE

Peter D. Zavitsanos, et al

General Electric Company

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Based on the exothermic nature of intermetallic reactions techniques have been developed which are capable of generating high temperatures in the condensed phase. By proper selection, based on the relative vapor pressures of all the components, it is possible to selectively vaporize metals for atmospheric release applications. Two intermetallic systems were successfully tested in the laboratory for the release of atom aluminum. They are:		

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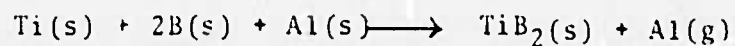
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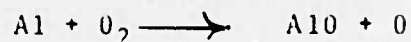
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Yields were determined for both reactions. The first reaction was utilized in releasing aluminum in the upper atmosphere at altitudes 145 Km and 125Km. Observations were made on the A10 clouds which were presumably formed by  $\text{O}_2$  attack on Al,



and subsequent photoluminescence of AlO by sunlight.

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METHODS FOR RELEASING METAL VAPORS  
IN THE UPPER ATMOSPHERE

Dr. Peter D. Zavitsanos  
Joseph A. Golden

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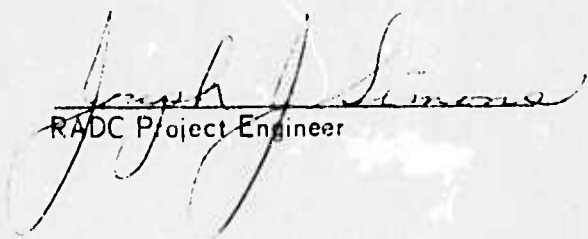
Project Engineer: Joseph J. Simons  
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This technical report has been reviewed and is approved.



RADC Project Engineer

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## TABLE OF CONTENTS

	<u>PAGE</u>
I. INTRODUCTION. . . . .	1
II. THERMOCHEMISTRY OF INTERMETALLIC REACTIONS. .	2
III. EXPERIMENTAL. . . . .	3
A. Materials . . . . .	3
B. Laboratory Results . . . . .	3
IV. ATMOSPHERIC RELEASE OF ALUMINUM . . . . .	25
A. Experimental. . . . .	25
B. Results. . . . .	25
REFERENCES. . . . .	26



## LIST OF FIGURES

<u>FIGURE NO.</u>		<u>PAGE</u>
1	The Mass Spectrum of Al(g) from Pd-Al Bimetallic Reaction . . . . .	6
2	Aluminum Deposited Inside Glass Tube from Pd-Al Reaction . . . . .	7
3	Diagram of Experimental Arrangement for Chemical Plume Studies . . . . .	8
4	Densitometer Trace of Al-Pd Plume, $10^{-3}$ Torr air . . .	9
5	Densitometer Trace of Al-Pd Plume, 1 atm air . . . . .	10
6	Pyrofoil Payload (111 gms) . . . . .	13
7	Vacuum Chamber for Laboratory - Testing of Release Packages . . . . .	14
8	Testing of the Pd/Al Payload . . . . .	16
9	The Mass Spectrum of Al(g) from Ti-B Intermetallic Reaction . . . . .	17
10	The Ti/2B Reaction $a \rightarrow b + c$ . . . . .	18
11	X-Ray Diffraction Starting Material "a" . . . . .	19
12	X-Ray Diffraction Product "b" . . . . .	20
13	X-Ray Diffraction Final Product "c" . . . . .	21
14	Aluminum Release from the Ti/B System . . . . .	24
15	B&W prints of HSE film, f/87, F = 75mm, slant range approx. 170 km, 10 sec. exp. Emission identified as AlO fluorescence . . . . .	27

## LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
I	Intermetallic Reactions . . . . .	2
II	Aluminum Release from the Pd/Al System . . . . .	12
III	Aluminum Release from the Ti/B System . . . . .	23

## I. INTRODUCTION

Radiation emanating from reactions of metal atoms with atmospheric species has been a topic of interest for a number of years. Such reactions can best be studied when the metal is released in the atomic state in the absence of other products such as oxides or smoke. It was, therefore, the objective of this effort to develop a (metal vapor) release technique which is not based on metal oxidation in the solid state as some previous efforts were but on some other source of chemical energy.

## II. THERMOCHEMISTRY OF INTERMETALLIC REACTIONS

The Brewer-Engel Theory<sup>2,3</sup> which was successful in predicting the structure and stability of alloys shows that reactions between metals in the condensed phase can be exothermic by as much as 80 kcal/mole. More recent experimental work by Cocke and Gingerich<sup>4</sup> has shown that CePd can be formed exothermically with the release of 78.6 kcal/mole.

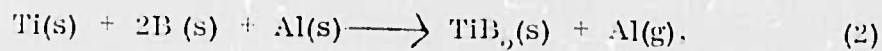
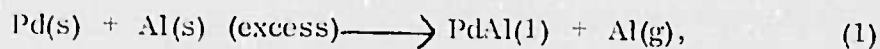
Experimental work on the Pd-Al system suggests that the reaction between these two elements is exothermic by 40 kcal/mole. Further search into the thermochemistry of intermetallic reactions<sup>6</sup> suggests the possibility of several reacting partners as being capable of generating high temperatures in the condensed phase. Table I shows several such combinations which can, in principle, generate adiabatic temperatures in excess of the boiling point of aluminum. The prediction, therefore, is that, if aluminum powder was placed in the Ti/B system or in excess in the Pd/Al system, it should be possible to end up with practically pure aluminum vapor since everything else will remain in the condensed phase

TABLE I  
INTERMETALLIC REACTIONS

<u>System</u>	<u>kcal</u> <u>mole</u>	<u>cal</u> <u>gm</u>	<u>cal</u> <u>cm<sup>3</sup></u>	<u>Adiabatic Reaction</u> <u>Temp. °C</u>
NiAl	-28.1	-329	-1,710	1639 (1)
PdAl	-43.7	-327	-2,890	2500 (1)
PLAl	-48	-216	-2,510	2800 (1)
TiB <sub>2</sub>	-71.6	-1,155	-4,040	3770 (1)
ZrB <sub>2</sub>	-78	-690	-3,330	3400 (1)
Hf B <sub>2</sub>	-78.6	-394	-3,450	3380 (1)
HfC	-52.3	-268	-2,730	4200 (s)

due to large differences in the respective vapor pressures.<sup>5</sup>

The proposed systems for study then are :



### III. EXPERIMENTAL

#### A. Materials

In the case of the Pd/Al system the materials used were Pd(70%) - Al(30%) in a sandwich form with palladium placed on the outside. The Ti/B reaction was evaluated with titanium powder 44/<sup>μ</sup> (average size) obtained from Ventron (Beverly, Mass.) and amorphous boron powder .04/<sup>μ</sup> (average size) supplied by Callery Chemical (Callery, Pa). The aluminum powder added to the stoichiometric mixture (TiB<sub>2</sub>) was 44/<sup>μ</sup> (average size) and furnished by Ventron. Formulations involving acrylic binders as well as several sinisiter-ing techniques were tested. Binders in general created smoking problems and low yields.

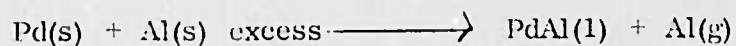
#### B. Laboratory Results

In order for the above schemes to be of practical interest the following criteria must be satisfied.

1. Reaction can be easily initiated.
2. Once initiated the reaction must be self-sustained at a fast rate.
3. The realized temperatures must be high enough to vaporize aluminum.
4. Production of high aluminum yields at a reasonable cost.
5. The system must be scalable to large (multi-killogram) quantities.
6. The reaction should not be explosive.

a. Pd/Al System

When a small portion of a Pd(70%) - Al (30%) pyrofoil is heated to a glowing temperature the mixture reacts violently and exothermically resulting in deflagration without the need for oxygen. The reaction being



produces liquid PdAl(l) and gaseous aluminum. Experimental substantiation of the usefulness of the above scheme in the production of pure aluminum vapor was achieved by the following observations:

1. The 70% Pd 30% Al pyrofoil was placed in a crucible and heated by an induction heater in vacuum. When the temperature of the crucible reached 625°C the sample flashed violently with the production of a molten residue and metallic coating on the walls of the vessel.

2. Repeating the experiment in a differentially pumped time-of-flight mass spectrometer it was observed that mass peak 27 is the main gaseous product of the reaction and, in fact, when care was exercised in keeping the sample and the container clean, mass peak 27 is the only signal resulting during the flash. Subsequent measurements related to the appearance potential of mass peak 27 unequivocally identified aluminum as the only major gaseous product of the reaction. Mass spectra of instrument background and Al-vapor produced during the flash are shown in Figure 1.

3. When a glass slide was placed between the sample and the ion source of the mass spectrometer Al vapor condensed on the glass and produced a fine mirror. A typical Al coating is shown in Figure 2.

4. The vapor generated in the crucible by this reaction was examined with a 1.5 meter B&L spectrograph as shown in Figure 3. At  $10^{-3}$  torr air the aluminum resonance lines ( $3944\overset{\circ}{\text{\AA}}$  and  $3961\overset{\circ}{\text{\AA}}$ ) show up quite strong while no palladium lines are detected. Figure 4

When the experiment was repeated at 1 atm air in addition to the aluminum lines the AlO band system appeared. Figure 5

Conducting thermochemical calculations on the Pd-Al system using a heat of reaction of 40 kcal/mole (of Pd reacting<sup>6</sup>), heat capacities for Al and Pd as given by Stall<sup>5</sup> and Sinke and a heat of vaporization of Al equal to 77.5 kcal/mole then the reaction:



can be written in a balanced form i. e., this system is capable of bringing its temperature to  $2700^{\circ}\text{K}$  (b.p. of Al) and vaporizing 10% of all Al present.

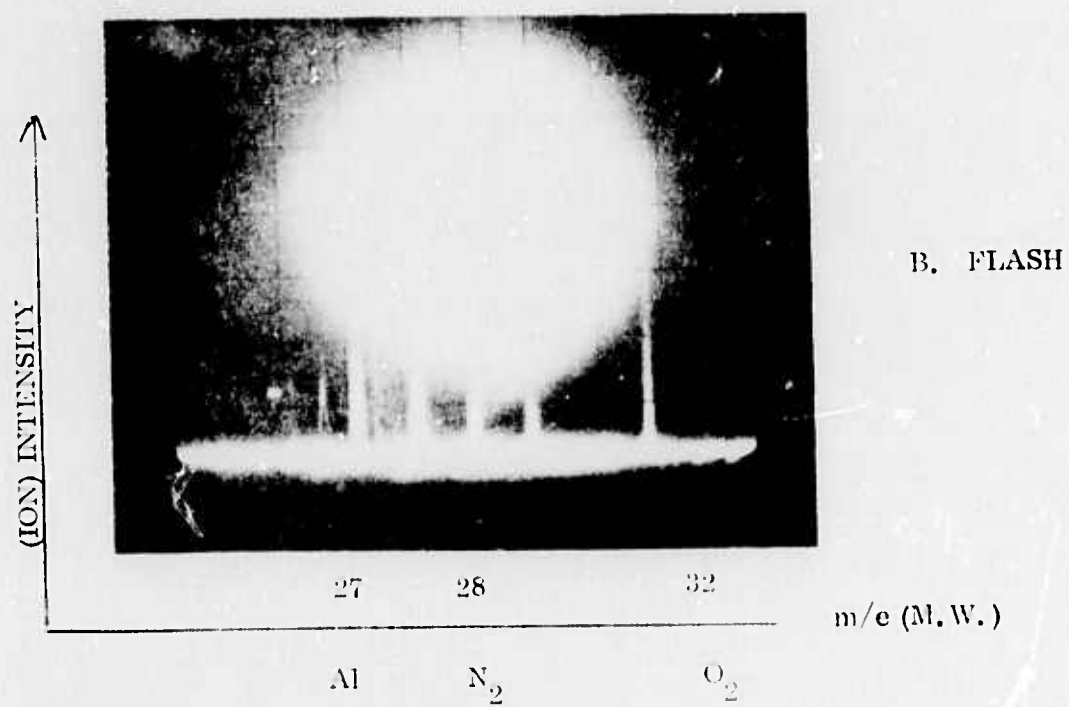
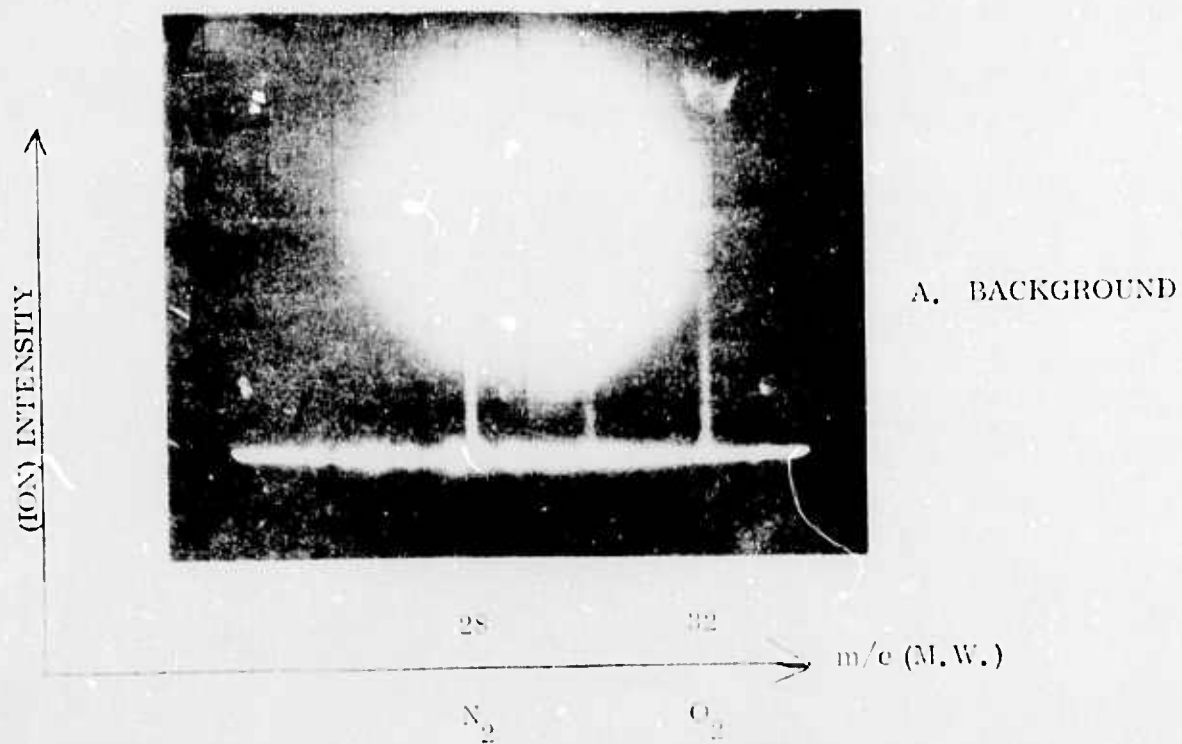


Figure 1. The Mass Spectrum of Al(g) from Pd-Al Bimetallic Reaction

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Figure 2. Aluminum Deposited Inside Glass  
Tube from Pd-Al Reaction



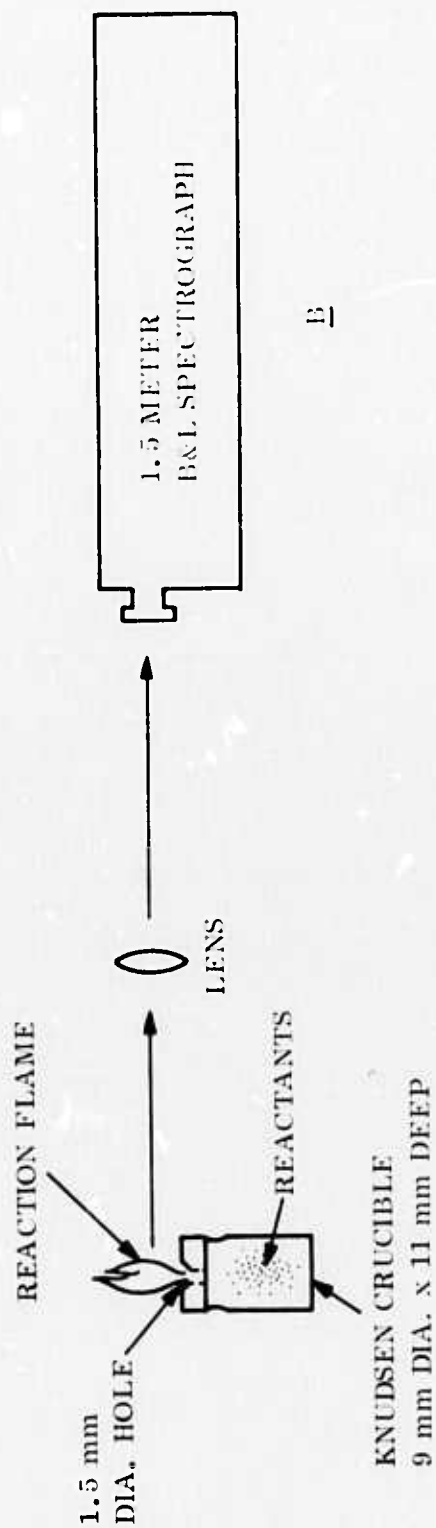
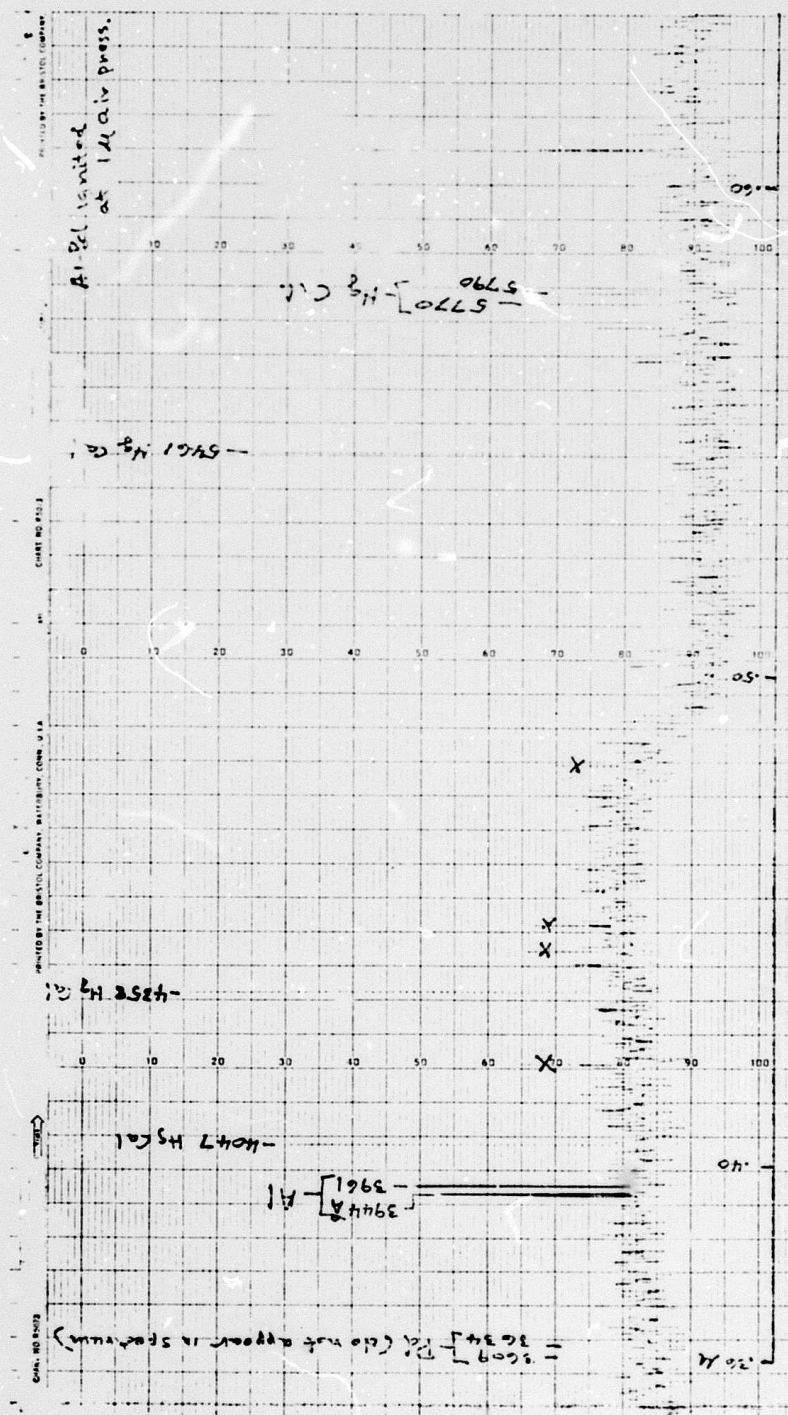


Figure 3. Diagram of Experimental Arrangement for Chemical Plume Studies.



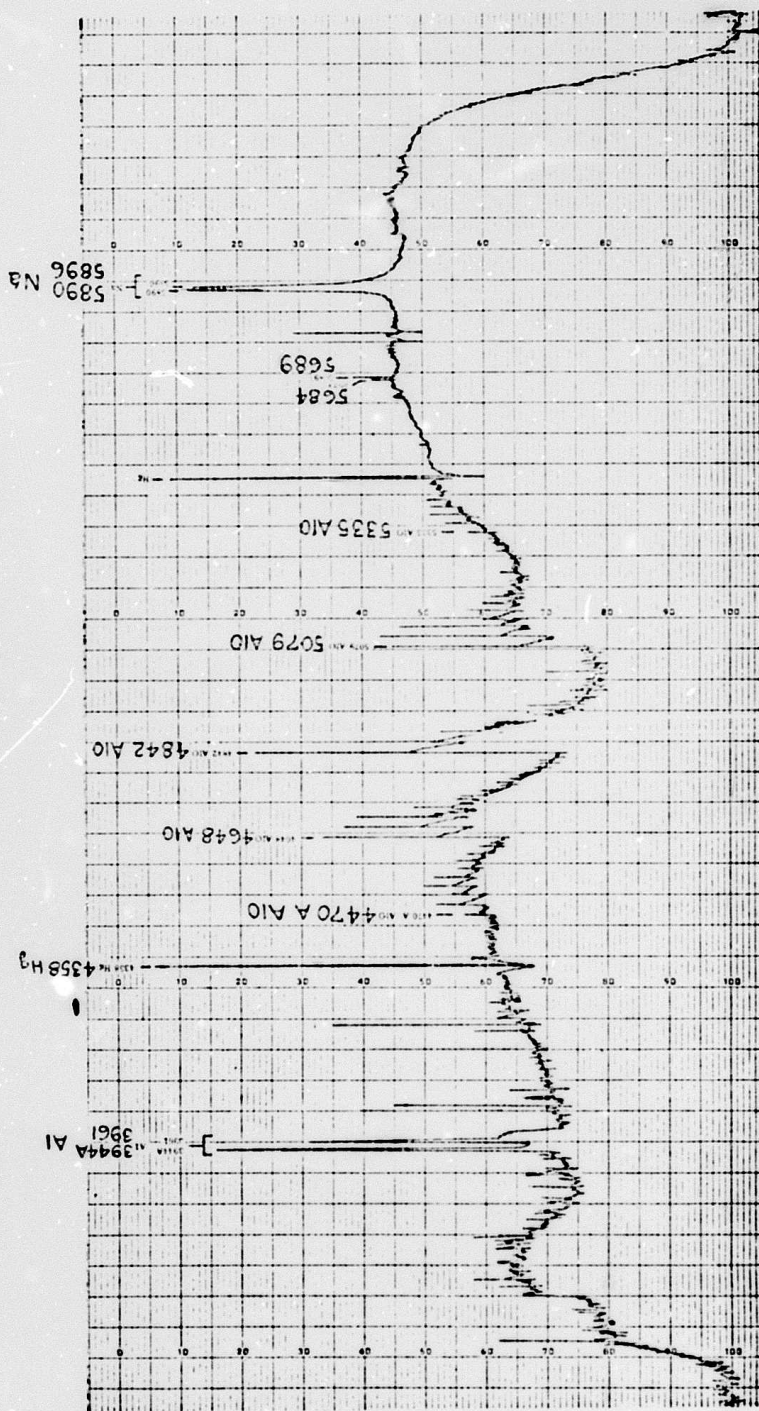


Figure 5. DENSITOMETER TRACE OF AI-Pd PLUME, 1 ATM AIR

In an effort to test this prediction experimentally several sample sizes were tested for yield in an attempt to scale up the process to atmospheric release packages. Flame emission spectrometry on the residue and target collection techniques on the resulting vapor were used for analysis and the conclusion to date is that the yield of Al(g) based on total weight is  $7.1 \pm 3\%$ . Data for samples ranging in size from 0.12 gm-111 gm are shown in Table II.

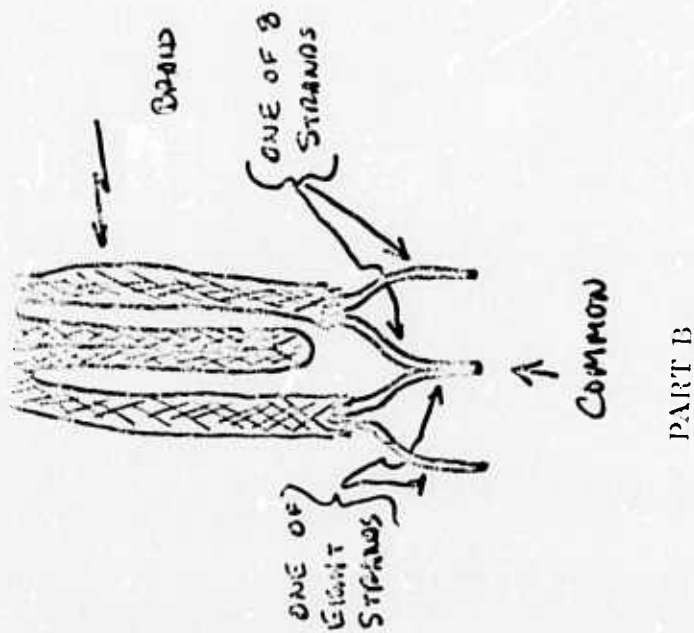
Since the 111 gm package was subsequently used in an atmospheric release experiment it will be discussed further. A diagram is shown in Figure 6. The reaction is initiated by supplying electrical power (20V, 27 Amps) to the braid arrangement shown on Figure 6 part B, which is a portion of part A. This package was tested prior to flight in a 5-ft. long vacuum chamber, Figure 7. The event was followed with a "Fastex" 16mm camera and three frames are included in this report as Figure 8.

TABLE II

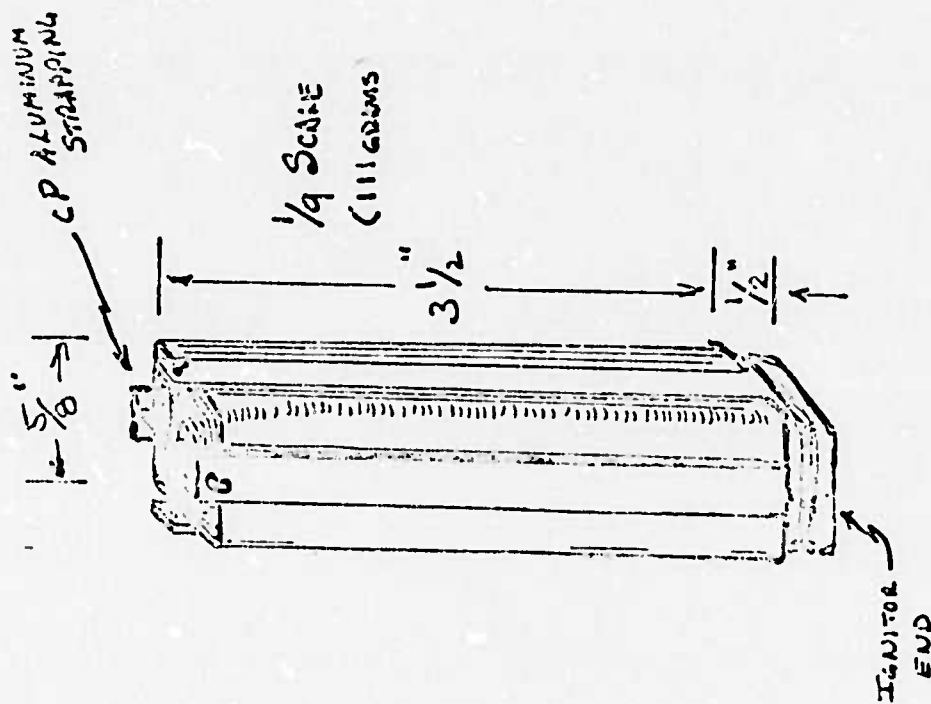
ALUMINUM RELEASE FROM THE Pd/Al SYSTEM

<u>REACTION</u>	<u>SIZE (g)</u>	<u>ANALYTICAL METHOD</u>	<u>WT. % RELEASED AS Al (g)</u>
Pd(s) + Al (s) - XCS → PdAl(l) + Al(g)	0.12	Flame Emission Spectrometry (NBS on residue)	6.2 - 14
"	0.974	Target Collection (of vapor)	9.47
"	1.03	"	2.72
"	27	"	6.4
"	111	"	4.1
		Ave.	7.1 ± 3





PART B



PART A

Figure 6. Pyrofoil Payload (111 gms)

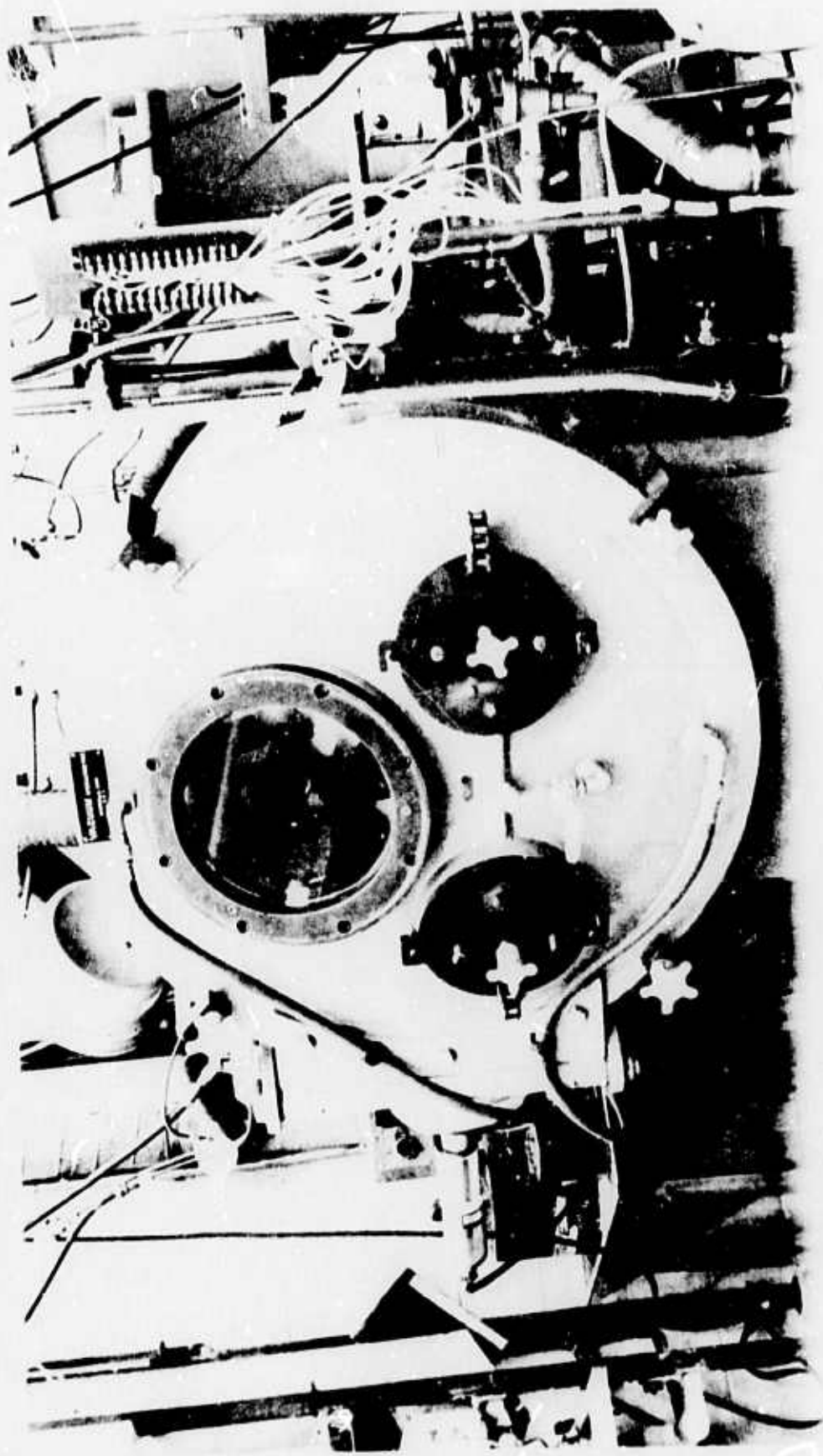


Figure 7. Vacuum Chamber for Laboratory - Testing of  
Release Packages

Frame A depicts the beginning of the reaction showing that the payload releases small droplets of PdAl (1) from both ends. Frame B corresponds to 200 msec later and shows that at this point the reaction has consumed about 30% of the payload. Frame C was taken at the end (700 msec from the start) showing the whole payload converted into small droplets each of which is acting as a source of aluminum vapor.

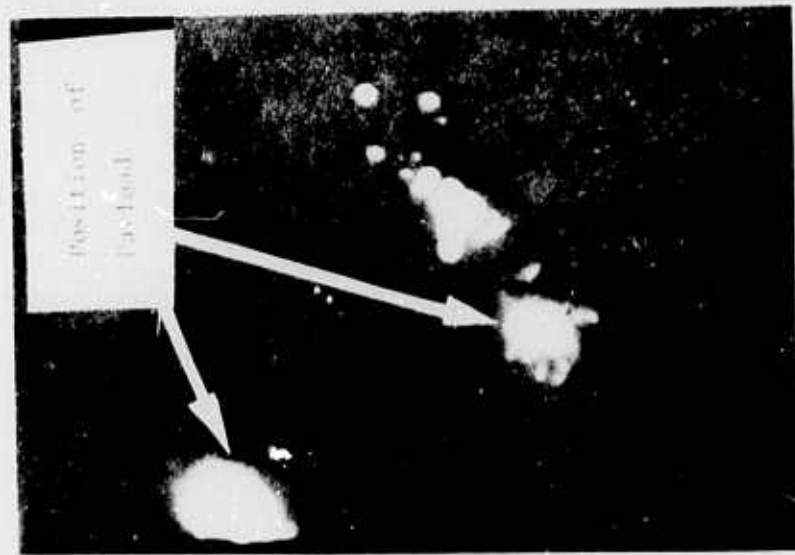
b. Ti/B System

Our search for other energetic systems as shown in Table I has suggested that based on thermochemistry the reaction between titanium and boron does indeed deserve further consideration. Formulations were made (with 20% aluminum) as previously described and tested.

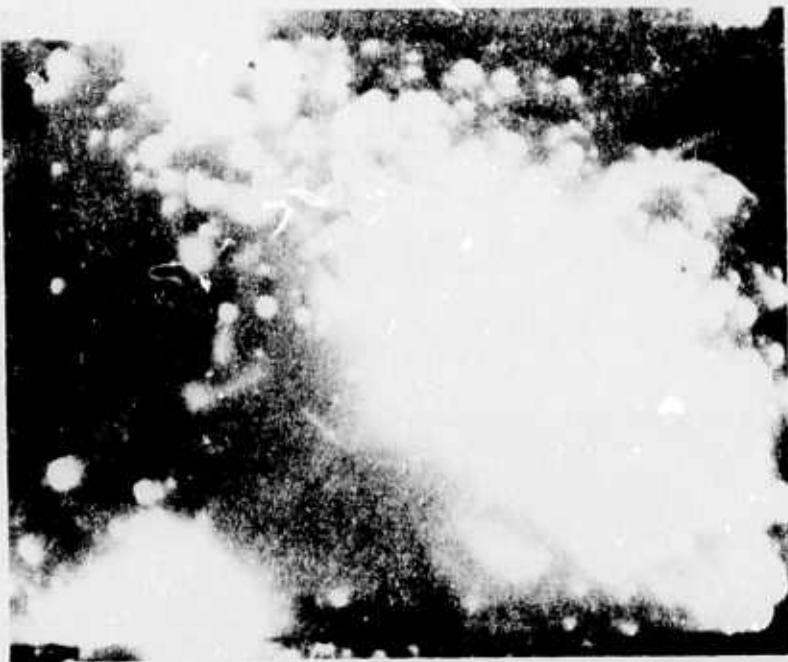
Items of interest which became immediately apparent are that this system too can be initiated simply, is self-sustaining at a fast rate, and does indeed produce aluminum vapor at a low cost. Heating locally a very small fraction of the mixture to 650°C starts the reaction and as Figure 9 shows the main gaseous product, as recorded by mass spectrometry, is Al (g).

A post mortem examination of the event is shown in Figure 10. Firing sample "a" produces a metallic coating "b" on the walls of the vacuum system and a finely divided residue "c". X-ray diffraction studies of the starting material "a" (Figure 11) shows the presence of all three elements (Ti, Al, B). Figure 12 is the diffraction pattern of the film (Product "b") which coats the walls of the vessel and appears to be essentially aluminum. The diffraction pattern of the residue product "c" Figure 13 matches that of  $TiB_2$  with no indication of free Ti present. Thus suggesting that the reaction went to near completion.

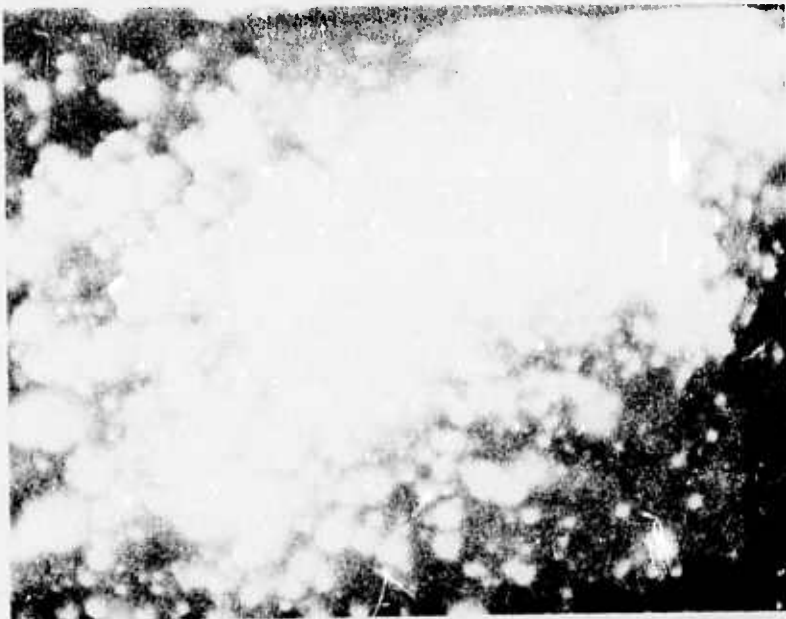




A. Beginning of ignition



B. 200m sec later



C. Reaction completed at 700m sec

Figure 8. Testing of the Pd/Al Payload

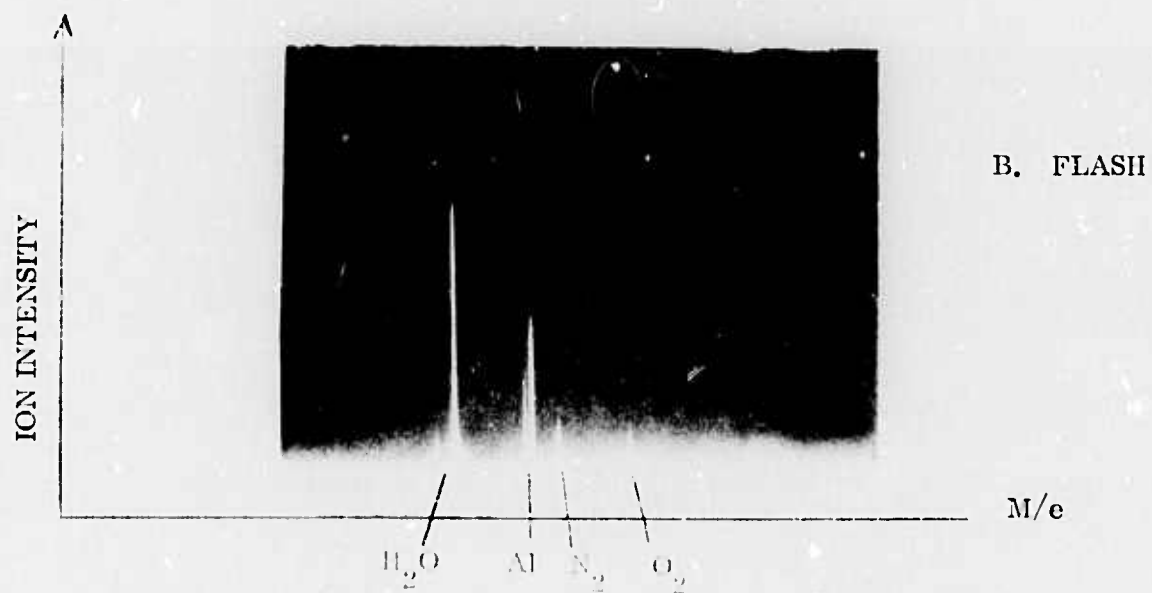


Figure 9. The Mass Spectrum of Al (g) from Ti-B Intermetallic Reaction.

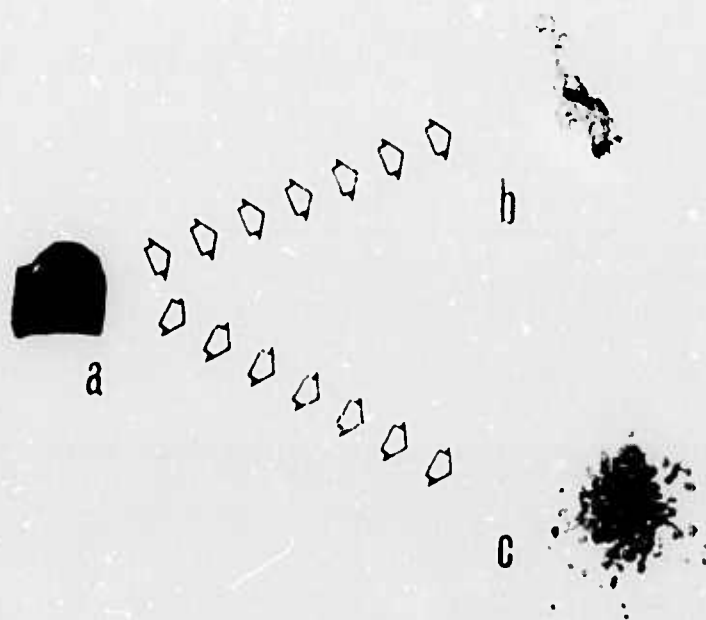


Figure 10. The Ti/2B Reaction

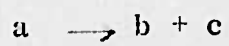


FIGURE 11. X-RAY DIFFRACTION STARTING MATERIAL "a"

TITANIUM + BORON + ALUMINUM

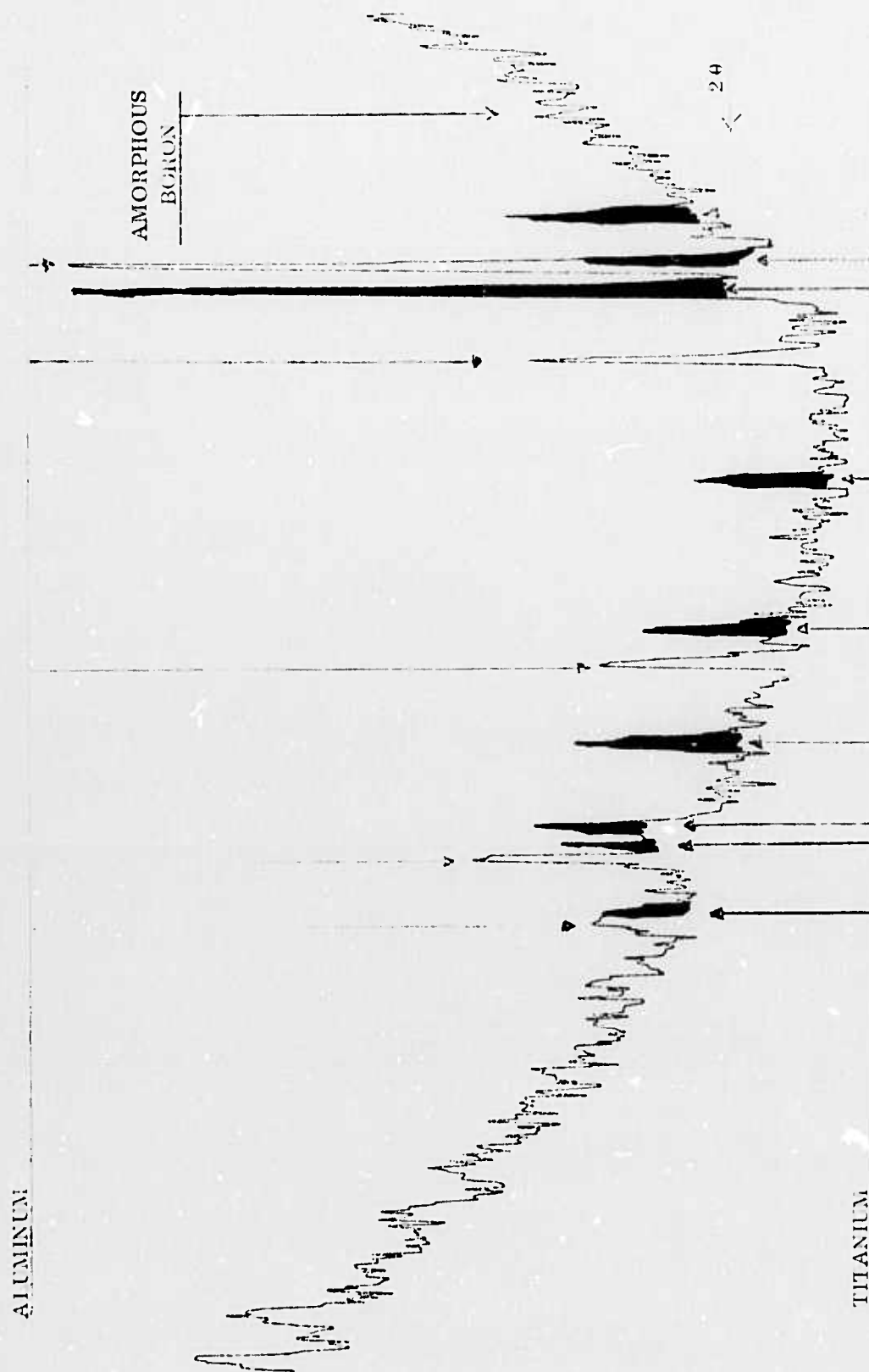


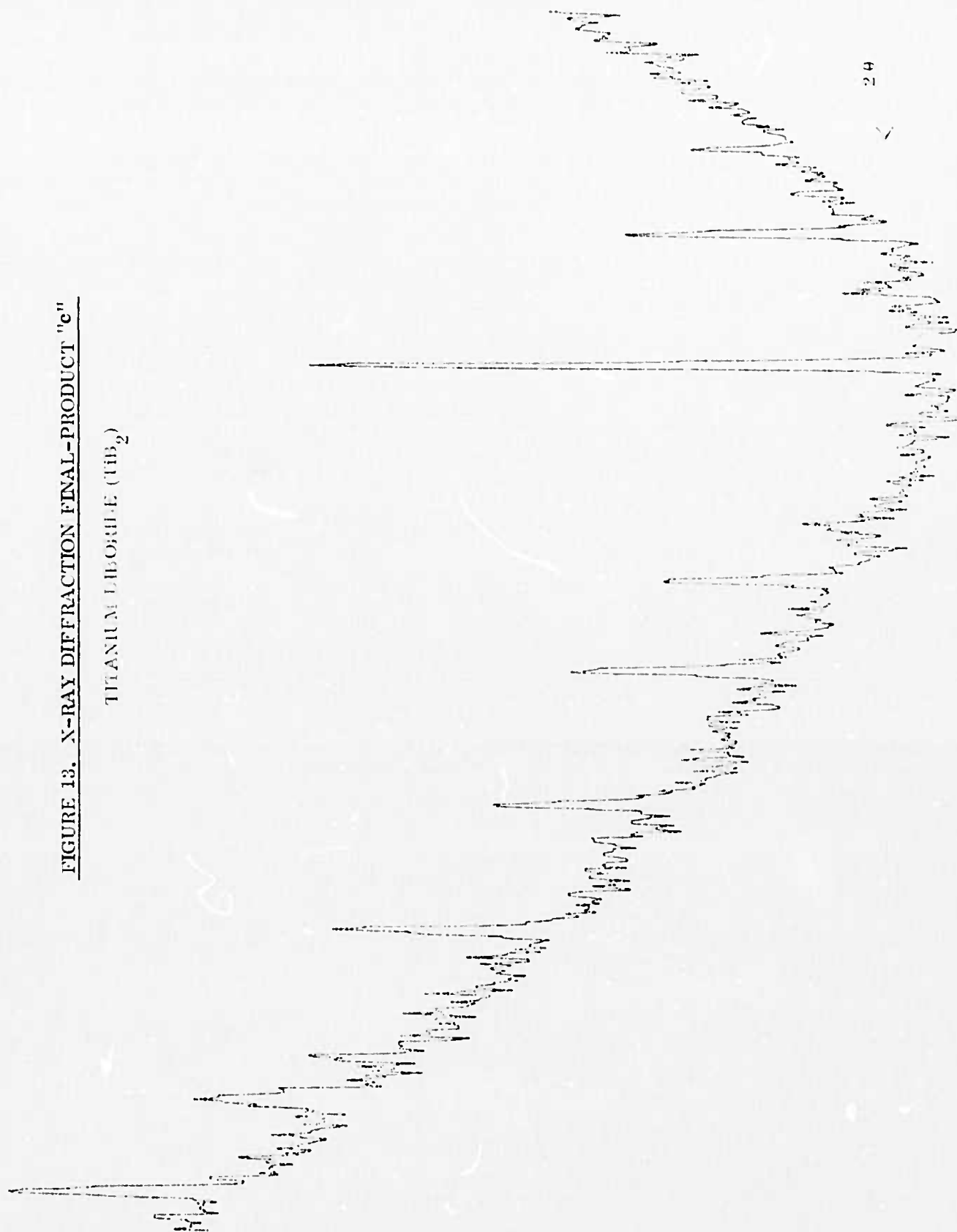
FIGURE 12. X-RAY DIFFRACTION PRODUCT "b"

ALUMINUM



FIGURE 13. X-RAY DIFFRACTION FINAL-PRODUCT "c"

TITANIUM LACONITE ( $\text{TiB}_2$ )



Yield measurements based on total weight are shown in Table III. The range for recovered aluminum is 4.8 - 11%. In addition to aluminum it appears that titanium is also generated in the vapor; its quantity is about a factor of ten less than aluminum.

Tests in the five-foot tank showed that the reaction can be initiated with a 20V, 27 A power supply (actual power requirement is probably much less) and progresses at a fast rate, i. e. , 100 gm sample lasts less than 1 second. Figure 14 shows two frames of the event: Frame A represents the beginning of the reaction, frame B is taken 100 m sec later. In observing the total event on film it is apparent that the reaction starts at the point of contact with the hot wire and propagates inward thus producing hot particles of  $TiB_2$  which individually act as sources of aluminum vapor.

TABLE III

ALUMINUM RELEASE FROM THE Ti/B SYSTEM

<u>REACTION</u>	<u>SIZE (g)</u>	<u>ANALYTICAL METHOD</u>	<u>WT. % RELEASED</u>
Ti(s) + 2B(s) + Al(s) - 20%	1	Atomic Absorption Spectrophotometry (collected coating)	6.4 Al 0.6 Ti
— / TiB <sub>2</sub> (c) + Al(g)			
"	2	"	4.8 Al 0.45 Ti
"	100	Target Collection of Vapor	11 Al





A. Beginning of Reaction



B. 100 msec later

Figure 14. Aluminum Release from the Ti/B System

#### IV. ATMOSPHERIC RELEASE OF ALUMINUM

##### A. Experiment

Two payloads consisting of 111 gm Pd/Al (each) identical to that previously described were hot wire ignited at 145 Km and 125 Km on the down leg of an AFCRL experimental research rocket.

The experiment was performed at Eglin, Fla. on October 19, 1973, at 1842 LT (twilight). A portion of the generated aluminum vapor was allowed to vent into the atmosphere through a 3.7 cm orifice on the skin of the rocket. Because of the geometry involved, it's expected that somewhere between 10-20% of the available vapor was released into the atmosphere. This in combination with the yield obtained from the laboratory measurements, it is estimated that 0.4 gm - 0.8 gm were released at each of the two altitudes.

##### B. Results

The releases were illuminated by sunlight and were observed by a camera at 170 Km slant range,  $F = 76$  mm,  $f/0.87$ , 35 mm Kodak 2475 film, 10 sec exposure.

The observations definitely established that the GE-payloads produced observable and photographable cloudlets as shown in Figure 15. Some of the data are:

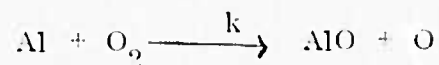
- a) Each cloud formed within 1-3 seconds after respective programmed release times.
- b) The lower cloud (125 km) was visually brighter than the upper one.
- c) The lower cloud grew to a diameter of approximately 1 km within ten seconds and to 1.6 km at 85 seconds. This suggests a diffusion coefficient of  $\sim 5 \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$  which is in the right range for an altitude of 125 km.

This cloud in turn dissappeared below film threshold at 200 seconds after release.

- d) The radiation consisted of AIO bands from  $B^2\Sigma^- \rightarrow X^2\Sigma^-$  photoluminescence.

e) There was no evidence of AlI resonance emission at 3944<sup>0</sup><sub>A</sub>.

In conclusion, since the lower cloudlet was brighter than the upper and three body collisions (involving Al + O + M) are unlikely at these altitudes it is suggested that AlO was formed through the reaction.



The rate constant for this reaction was measured in the laboratory by Fontijn<sup>7</sup> and is rather high ( $k = 3 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ ). The absence of AlI resonance lines is somewhat puzzling in view of the fact that the release event involves hot atomic aluminum which can radiate thermally as well as through sunlight excitation. Without additional information on the relative sensitivity of the instruments involved no conclusion can be reached. It is hoped that future releases involving larger quantities will allow more detailed observations and more complete analyses.



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